Chapter-3

MERCURY EMISSIONS FROM ANTHROPOGENIC SOURCES: ESTIMATES AND MEASUREMENTS FOR EUROPE

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INTRODUCTION

Processing of mineral resources at high temperatures, such as combustion of fossil fuels, roasting and smelting of ores, kilns operations in cement industry, as well as incineration of wastes and production of certain chemicals result in the release of several volatile trace elements into the atmosphere. Mercury is one of the most important trace elements emitted to the atmosphere due to its toxic effects on the environmental and human health, as well as its role in the chemistry of the atmosphere.

Although substantial information has been collected on environmental effects of mercury and its behaviour in the environment much less data is available on atmospheric emissions of the element. Information on emissions is needed for various policy and modelling purposes. This need has been recognized not only locally where mercury may pose direct problems but also on regional scale because the element is a subject of long-range transport while in the atmosphere.

PARAMETERS AFFECTING EMISSIONS OF MERCURY FROM VARIOUS ANTHROPOGENIC SOURCES

There are four major groups of parameters affecting mercury emissions:

- contamination of raw materials by mercury,
- physico-chemical properties of mercury affecting its behaviour during the industrial processes,
- the technology of industrial processes, and
- the type and efficiency of control equipment.

Contamination of raw materials

Concentrations of mercury in coals and fuel oils vary substantially depending on the type of the fuel and its origin, as well as the affinity of the element for pure coal and mineral matter. The sulphide-forming elements, with mercury included, are consistently found in the inorganic fraction of coal. Although it is very difficult to generalize on the impurities in coal, the literature data seem to indicate that the mercury concentrations in coals vary between 0.01 and 1.5 ppm (a review in Pirrone et al., 2001). These concentrations are presented in Table 1. It should be noted that mercury concentrations within the same mining field might vary by one order of magnitude or more.

Table 1. Concentrations of Hg in various fossil fuels.

Fuel	Unit	Concentration
1. Hard coals	g/tonne	
- Europe		0.01-1.5
- USA		0.01-1.5
- Australia		0.03-0.4
- South Africa		0.01-1.0
- Russia		0.02-0.9
- Brown coals	g/tonne	
- Europe		0.02-1.5
USA		0.02-1.0
3. Crude oil		0.001-0.05
4. Natural gas	mg/m^3	0.01-5.0*

(*) A reduction of Hg to concentrations lower than 10 $\mu g/m^3$ must be obtained before the gas can be used.

There is only limited information on the content of mercury in oils. In general, mercury concentrations in crude oils range from 0.01 to as much as 30.0 ppm (Pacyna, 1987). It is expected that mercury concentrations in residual oil are higher than those in distillate oils being produced at an earlier stage in an oil refinery. Heavier refinery fractions, including residual oil, contain higher quantities of ash containing mercury.

Natural gas may contain small amounts of mercury but the element should be removed from the raw gas during the recovery of liquid constituents, as well as during the removal of hydrogen sulphide. Therefore, it is believed that mercury emissions during the natural gas combustion are insignificant.

Mercury appears as an impurity of copper, zinc, lead, and nickel ores. Obviously, there are also mercury minerals, particularly cinnabar. The element is also present in the gold ores. It is very difficult to discuss the average content of mercury in the copper, zinc, lead, nickel and gold ores as very little information is available in the literature on this subject. Average zinc ores contain larger amounts of the element compared to copper and lead ores (Pacyna, 1983).

Chemical composition of input material for incineration is one of the most important factors affecting the quantity of atmospheric emissions of various pollutants from waste incineration. Very limited information exists on mercury concentrations in various types of wastes. Another difficulty is that it is almost impossible to calculate an average value for these concentrations due to the high variabilities in the content and origin of wastes to be incinerated, even in the same incinerator. Therefore, it is rather difficult to extend the information on the mercury content measured in one incinerator for another one.

Physico Chemical Properties of Mercury Affecting its Behaviour during the Industrial Processes

Most of the processes generating atmospheric emissions of mercury employ high temperature. During these processes, including combustion of fossil fuels, incineration of wastes, roasting and smelting operations in non-ferrous and ferrous metallurgy, and cement production, mercury introduced with input material volatilizes and is converted to the elemental form. It has been confirmed in various investigations that almost 100 % of the element is found in exhaust gases in a gaseous form, as discussed later in this paper.

Technology of Industrial Processes

Various technologies within the same industry may generate different amounts of atmospheric emissions of mercury. It can be generalized for conventional thermal power plants that the plant design, particularly the burner configuration has an impact on the emission quantities. Wet bottom boilers produce the highest emissions among the coal-fired utility boilers, as they need to operate at the temperature above the ash -melting temperature. The load of the burner affects also the emissions of trace elements including mercury in such a way that for low load and full load the emissions are the largest. For a 50 % load the emission rates can be lower by a factor of two.

The influence of plant design or its size on atmospheric emissions of mercury from oil-fired boilers is not as clear as for the coal-fired boilers. Under similar conditions the emission rates for the two major types of oil-fired boilers: tangential and horizontal units are comparable.

Non-conventional methods of combustion, such as fluidized bed combustion (FBC) were found to generate comparable or slightly lower emissions of mercury and other trace elements than the conventional power plants (e.g. a review in Pirrone et al., 2001). However, a long residence time of the bed material may result in increased fine particle production and thus more efficient condensation of gaseous mercury.

Among various steel making technologies the electric arc (EA) process produces the largest amounts of trace elements and their emission factors are about one order of magnitude higher than those for other techniques, e.g., basic oxygen (BO) and open hearth (OH) processes. The EA furnaces are used primarily to produce special alloy steels or to melt large amounts of scrap for the reuse. The scrap which often contains trace elements, and on some occasions mercury, is processed in electric furnaces at very high temperatures resulting in volatilization of trace elements. This process is similar from the point of view of emission generation to the combustion of coal in power plants. Much less scrap is used in other furnaces, where mostly pig iron (molten blast-furnace metal) is charged. It should be noted, however, that the major source of atmospheric mercury related to the iron and steel industry is the production of metallurgical coke.

Quantities of atmospheric emissions from waste incineration depend greatly on the type of combustor and its operating characteristics. The mass burn/waterwall (MB/WW) type of combustor is often used. In this design the waste bed is exposed to fairly uniform high combustion temperatures resulting in high emissions of gaseous mercury and its compounds. Other types of combustors seem to emit lesser amounts of mercury as indicated by the comparison of the best typical mercury emission factors for municipal waste combustors (MRI, 1993). It is also suggested that fluidized-bed

combustors (FB) emit smaller amounts of mercury to the atmosphere compared to other sewage sludge incineration techniques, and particularly multiple hearth (MH) techniques.

Type and Efficiency of Control Equipment

The type and efficiency of control equipment is the major parameter affecting the amount of trace elements released to the atmosphere. Unlike other trace elements, mercury enters the atmosphere from various industrial processes in a gas form. The application of flue gas desulfurisation (FGD) has a very important impact on removal of mercury. A number studies have been carried out to assess the extend of this removal and parameters having major impact on this removal. These studies were reviewed in connection with the preparation of the EU Position Paper on Ambient Air Pollution by Mercury (Pirrone et al., 2001). It was concluded that the relatively low temperatures found in wet scrubber systems allow many of the more volatile trace elements to condense from the vapour phase and thus to be removed from the flue gases. In general, removal efficiency for mercury ranges from 30 to 50%. It was also concluded that the overall removal of mercury in various spray dry systems varies from about 35 to 85%. The highest removal efficiencies are achieved from spray dry systems fitted with downstream fabric filters.

Table 2. Emission factors for Hg, used to estimate European emissions of the element to the atmosphere in 2000.

Category	Unit	Emission factor
Coal combustion:	g/tonne coal	
- power plants		0.1-0.3
- residential and commercial boilers		0.5
Oil combustion	g/tonne oil	0.006
Non ferrous metal production		
- Cu smelters	g/tonne Cu produced	5.0-6.0
- Pb smelters	g/tonne Pb produced	3.0
- Zu smelters	g/tonne Zu produced	7.5-8.0
Cement production	g/tonne cement	0.1
Pig iron % steel production	g/tonne steel	0.04
Waste incineration	g/tonne wastes	
Municipal wastes		1.0
Sewage sludge wastes		5.0

EMISSION ESTIMATES

Emission estimates are carried out on the basis of information on emission factors and statistics on the production of industrial goods and the consumption of raw materials.

Emission factors are prepared for each source sector and raw material, separately. They can be evaluated on the basis of measurements or mass balance estimates for mercury during certain industrial process or certain application of the element.

The emission factors used for the estimates of the European emissions of Hg in the reference year 2000 are presented in Table 2.

The European emissions from anthropogenic sources in the year 2000 are presented in Table 3. These estimates were made with the use of emission data provided by national experts from a number of European countries. The emission factors from Table 2 were used for estimates for the rest of the European countries.

It can be concluded that a half of the European emissions in the year 2000 is emitted during combustion of fuels.

The second category consists of several industrial processes, including chlor-alkali production, non-ferrous and ferrous metal production and cement production. Other sources include waste incineration and various uses of mercury.

Table 3. Changes in total anthropogenic emissions of mercury in Europe since 1980 (in tonnes/year).

Source category	1980	1985	1990	1995	2000
Combustion of fuels	350	296	195	186	114
Industrial processes	460	388	390	143	99
Other sources	50	42	42	59	26
Total	860	726	627	338	239

Data in Table 3 also indicate steady decrease of Hg emissions in Europe during the last 2-3 decades. Major decline of Hg emissions in Europe occurred at the end of the 1980's and the beginning of the 1990's.

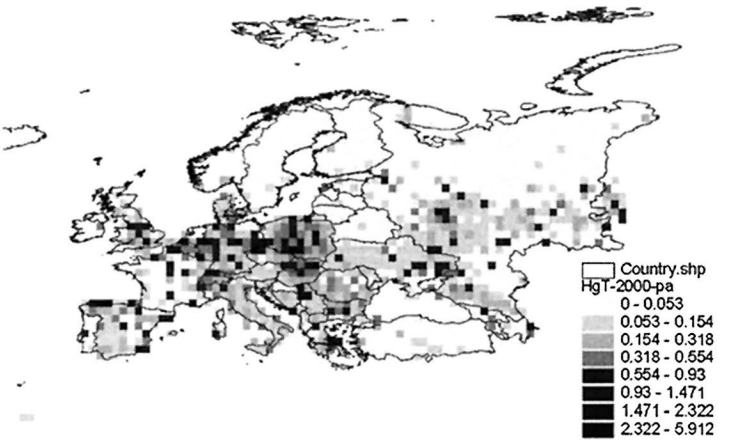

Figure 1. Spatial distribution of Hg emissions from anthropogenic sources in Europe in 2000 within the 50 km x 50 km grid (in t/grid).

This decrease was caused mainly by 1) the implementation of the FGD equipment in large power plants and the other emission controls in other industrial sectors, particularly in Western Europe, and 2) decline of economy in Eastern and Central Europe due to the switch in economies in these countries from centrally planned to market oriented.

Information on emissions from individual point sources and geographical location of these sources was then used to prepare Hg emission maps for Europe. The area source emissions, such as the emissions during combustion of fuels to produce heat in residential boilers were spatially distributed using the population density map as a surrogate parameter. The map for Hg emissions in 2000 from anthropogenic sources in Europe within the grid system of 50 km by 50 km is presented in Figure 1.

The areas where coal combustion is the main source of energy production are the regions with the highest emissions of mercury.

Estimates of emissions of mercury in its major physico-chemical forms were also approached (e.g. Pacyna et al., 2001). A summary of this work is presented in Table 4 in a form of Hg emission profiles for major emission sectors with regard to the three forms: elemental gaseous, bivalent gaseous, and elemental Hg on particles.

Table 4. Emission profiles of Hg from anthropogenic Sources.

Species	Coal combustion		Oil combustion	Non-Ferrous Metals		Pig & Iron	Caustic Soda	Waste Disposal	Other	Average	Source
	Power plants	Res. heat		Pb	Zn						
Hg^0 (gas)	0.5	0.5	0.5	0.8	0.8	0.8	0.7	0.2	0.8	0.64	Modified Pacyna, 1998
Hg^{II}	0.4	0.4	0.4	0.15	0.15	0.15	0.3	0.6	0.15	0.285	
Hg (p)	0.1	0.1	0.1	0.05	0.05	0.05	0	0.2	0.05	0.075	

EMISSION MEASUREMENTS

In order to improve the reliability of current estimates of atmospheric emissions of mercury, source test measurements of individual mercury species are required. With coal-fired power plants and waste incinerators being the dominant stationary anthropogenic sources of atmospheric mercury in Europe including the European Union and Eastern Europe, source test measurements in recent European projects have focused on stationary combustion sources. Concentrations of mercury associated with particulate matter, vapour phase elemental mercury, oxidised mercury and methyl mercury measured in stack gases of 7 fossil fuel-fired utility boilers and 3 thermal waste treatment facilities located in Europe are presented in this paper.

Emissions of mercury species from stationary combustion sources

Plant information

Within the two EU projects: "Optimal Utilisation of coal in modern power plants with respect to control of mass flows and emissions of VOCs/PAHs and mercury " (ECSC Coal Research Agreement No. 7220-ED/089) and "Mercury Species Over Europe (MOE) Mercury Species over Europe. Relative Importance of Depositional Methylmercury Fluxes to Various Ecosystems" (Contract ENV4-CT97-0595) (Munthe et al., 2001), measurements were carried out in ten stationary combustion sources.

Table 5. Main parameters for coal fired power plants reported in this chapter.

Source	Fuel	Output (electricity/total)	Stack gas cleaning technology
Power plant 1	Pulverised hard coal	170 850 MW	ESP
Power plant 2	Pulverised hard coal	150/270 MW	ESP, semi dry de-SOx, fabric filter
Power plant 3	Pulverised hard coal	640/340 MW	ESP, wet de-SOx, SCR
Power plant 4	Lignite	360/- MW	ESP
Power plant 5	Lignite	500/- MW	ESP
Power plant 6	Hard coal	170/ - MW	ESP
Power plant 7	Hard coal	330/ - MW	ESP, de SOx

Table 6. Main parameters for waste incinerators reported in the chapter.

Source	Waste type	Output (electricity/total)	Stack gas cleaning technology
Waste incinerator 1	Municipal waste	24 MW/ 400 000 GJ	ESP
Waste incinerator 2	Municipal waste	20/146 MW	ESP, wash reactor and condensing reactor, SNCR, fabric filter
Waste incinerator 3	Municipal waste	2*10 MW/120 GW	Cyclones, ESP, semi dry lime reactor, activated carbon feeding, fabric filter

The point sources were located in member states of the European Union and also in other European countries. All source test measurements were performed on the premises that the individual stationary combustion source may be kept anonymous. The measurement campaigns were performed in 1998-2000. A description of the point sources is given in Table 5 and 6 for coal fired power plants and waste incinerators, respectively.

Source test measurement methodology

Two different sampling approaches for the measurement of mercury in stack gases were employed. The MESA method and the modified standard test method were used for all stack gas measurements at all ten combustion sources. At two stationary point sources, an on-line speciation method and a denuder sampling method were also employed.

Six tests were usually conducted at each site. Samples were collected for 1-3 hours at gas flow rates of 0.5-2 l/min. During the test periods, operating data of the plant were obtained at each test site. After sampling, the solid and

liquid samples were sealed and stored in the dark. The collected mercury was analysed using cold vapour atomic fluorescence spectrometry (CV-AFS) or cold vapour atomic absorption spectrometry (CV-AAS). Based on analytical results and operating data of each plant, mercury mass concentration in the stack was calculated. The concentrations of mercury species in the stack gases of the boilers measured are presented in Table 7 and 8 for coal fired power plants and waste incinerators, respectively.

These results suggest that vapour phase elemental mercury and oxidised mercury (mercury(II) chloride) are the dominant mercury species in stack gases from combustion sources equipped with both conventional and state-of-the-art flue gas cleaning systems. With the MESA method for vapour phase mercury speciation, the relative concentrations levels for vapour phase elemental mercury was found to be 41% for the coal-fired power plant equipped only with electrostatic precipitator and in the range from 0 to 53% for modern hard coal fired utility boilers. With the modified standard method, the relative concentration of elemental mercury vapour was found to be 43% for conventional hard coal fired power plants and from 43 to 75% for modern facilities. Traces of methylmercury were found in a few stack gas samples but the concentration fractions were always below 1% and are considered to be unreliable given the analytical difficulties in these complex samples. The conclusion is that waste incinerators and coal fired power plants are not sources of methylmercury emissions to air. Mercury associated with particulate matter was found to be also below 1% of total mercury in the flue gases. Lignite is an additional domestic fuel used in utility boilers in Europe. Emission estimates for mercury species released from conventional and modern brown coal fired power plants are presented in Table 7. Total mercury emission from a lignite fired power plant equipped only with electrostatic precipitator was found to be 26.9 μg Hg/m^3 (13.2 μg Hg/MJ) with the MESA and 10.4 μg Hg/m^3 (5.2 μg Hg/MJ) with the modified standard method. With the MESA method and the modified standard method, respectively, the concentration for total mercury in flue gas from a modern lignite fired power plant was found to be 5.1 μg Hg/m^3 (1.03 μg Hg/MJ) and 4.9 μg Hg/m^3 (0.98 μg Hg/MJ). It is concluded that the elevated concentration of total mercury from the conventional power plant is due to high mercury concentration in the lignite burned.

The calculated relative emissions of vapour phase elemental mercury was found to be from 61 to 99% for the conventional power plants and from 94 to 100% for the modern power plants. The relative concentration levels of mercury associated with particulate matter were found to be well below 1%.

Table 7. Concentrations of Hg in exhaust gas from coal fired power plants (MESA = Mercury Speciation and Adsorption method, MS = Modified standard method).

Source	Hg(II) μgm^{-3}		Hg^0 μgm^{-3}		Hg Tot μgm^{-3}		Emission factor (Tot Hg) µg/mJ	
	MESA	MS	MESA	MS	MESA	MS	MESA	MS
Power plant 1	2.6	2.7	1.8	2.0	4.4	4.7	1.9	1.2
Power plant 2	0.7	-	0	-	0.7	0.8	0.3	0.3
Power plant 3	2.1	0.8	2.4	2.4	4.5	3.2	1.9	2.0
Power plant 4	10.4	-	16.5	10.4	26.9	10.4	13	5.2
Power plant 5	0.3	0	4.8	4.9	5.1	4.9	1.0	0.98
Power plant 6	2.6	2.7	1.8	2.0	4.4	4.7	1.9	2.0
Power plant 7	0.8	-	0.6	-	1.4	-	-	0.61

Table 8. Concentrations of Hg from waste incinerators.

Source	Hg(II) μgm^{-3}		Hg^0 μgm^{-3}		Hg Tot μgm^{-3}		Emission factor (Tot Hg) mg/tonne waste	
	MESA	MS	MESA	MS	MESA	MS	MESA	MS
Waste incinerator 1	53.1	178	83.3	14	136	194	499	707
Waste incinerator 2	5.1	-	14.7	-	19.8	17.3	81	71
Waste incinerator 3	8	-	15.4	28.4	23.4	28.4	152	183

The concentration levels of total mercury in exhaust gases from waste incinerators were found to be 136 and 194 µg Hg/m^3 (499 and 707 mg Hg/ tonne waste burned) for waste incinerators equipped with only electrostatic precipitator and from 17 to 28 µg Hg/m^3 (71 to 183 mg Hg/tonne waste burned) for thermal waste treatment plant with state-of-the-art air pollution control technology. Measurements performed at thermal waste treatment facilities showed also that both vapour phase elemental mercury and oxidised mercury are the main mercury species released to the atmosphere.

For the vapour phase elemental mercury, the relative concentrations were found to be 61% for conventional waste incinerators and from 66 to 74% for modern facilities. From these results, it is concluded that the speciation pattern of vapour phase mercury deviate considerable from an expected relative proportion of Hg^0 estimated from thermodynamic equilibrium calculations. From the source test measurements, it is also concluded that methylmercury is very unlikely to be present in significant concentration

levels in stack gases from waste incinerator equipped with both conventional and state-of-the-art flue gas cleaning systems.

Comparison between measurements and estimates

A comparison of total mercury concentrations in the exhaust gases measured during the EU project on Mercury over Europe (MOE) and estimated during the EU project on the Mediterranean Atmospheric Mercury Cycle System (MAMCS) (http://www.cs.iia.cnr.it/MAMCS/project.htm) is presented in Table 9.

Table 9. Comparison of Hg emission measurements (the MOE project) with estimates (the MAMCS project).

Point source	**Country**	**Emission (Kg/yr)**	
		Measured	Emission Factor estimates
Power plant	Poland	2990	2140
Waste incinerator	Sweden	32.4	80
Power plant	Finland	8.2	50
Power plant	Poland	90	145
Waste incinerator	Hungary	191	250
Power plant	Germany	69.8	175

The estimates are generally higher than the measurements, but the difference is within a factor of 2 except for a power plant in Finland. It should be added, however, that many more measurements need to be performed in order to obtain conclusive results with regard to the applicability of currently available emission factors for emission estimates for Hg from anthropogenic sources.

FINAL REMARKS

During the last decade major progress has been made to assess emissions from anthropogenic sources in Europe. This work resulted in the improvement of our knowledge of emission factors and emissions in Europe, as well as in other parts of the world (e.g. Pacyna et al., 2003). It can be concluded that combustion of fossil fuels to produce electricity and heat is the major emission source in Europe and worldwide. Future emissions of Hg from anthropogenic sources can be expected to decrease due to wider

application of equipment for desulfurization in major power plants and industrial boilers, as well as wider use of renewable energy sources.

Source test measurement at both coal-fired power plants and waste incinerators in Europe have been performed to determine the concentration levels of mercury associated with particulate matter, and vapour phase elemental mercury, oxidised mercury and methylmercury in stack gases. Vapour phase elemental mercury and oxidised mercury are the main mercury species emitted form conventional and state-of-the-art stationary combustion sources. The relative proportion of mercury associated with particulate matter was found to be low for combustion sources equipped with both conventional and state-of-the-art flue gas cleaning installations. Methylmercury was found generally not occurring in stack gases from combustion sources.

More measurements of Hg emissions from at least major point sources are needed for making emission inventories more accurate. The measurements of Hg species in exhaust gases from these sources are also needed. Results obtained with current measurement methods were found to lie in the same order of magnitude for vapour phase elemental mercury and oxidised mercury. However, it is not conclusive whether the sampling methods determine the mercury species correctly.

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